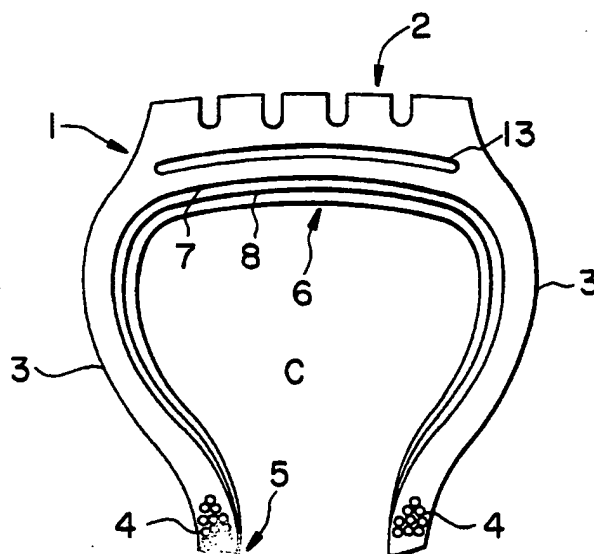




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B60C 1/00, B32B 27/06 C08K 5/47	A1	(11) International Publication Number: WO 92/20538 (43) International Publication Date: 26 November 1992 (26.11.92)
(21) International Application Number: PCT/US92/02417 (22) International Filing Date: 25 March 1992 (25.03.92) (30) Priority data: 705,224 24 May 1991 (24.05.91) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: DOLLINGER, Susan, E. ; 257 Clouse Lane, Granville, OH 43023 (US). DAVIS, William, H., Jr. ; 13944 Shenandoah, Baton Rouge, LA 70815 (US). (74) Agent: ANAND, Mona; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AT (European patent), AU, BE (Euro- pean patent), CA, CH (European patent), DE (Euro- pean patent), DK (European patent), ES (European pa- tent), FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (Eu- ropean patent), SE (European patent). Published <i>With international search report.</i>

(54) Title: ELASTOMERIC BARRIER FILMS FOR TIRES**(57) Abstract**

Disclosed is at least a two-layered chlorinated polyethylene film for use as an inner liner for a pneumatic rubber substrate or a tire, with an inner layer adjacent an inner surface of the rubber substrate comprising an adhesive resin; and an outer layer consisting essentially of chlorinated polyethylene containing from 35 to 50 % by weight chlorine, a derivative of 2,5-dimercapto 1-3,4 thiadiazole as a curative, an accelerator, an acid acceptor, and optionally containing carbon black. The film is from 0.13 mm (5 mil) to 0.76 mm (30 mil) in thickness, and has oxygen permeability from 6×10^{-12} to 36×10^{-12} cc-cm/cm²-cmHg-sec (10 to 60 cc-mil/100 sq.in.-atm-day). The film containing carbon black typically has an intermediate layer of a thermoplastic elastomer interposed between the adhesive layer and CPE layer. Further disclosed is a pneumatic rubber substrate or a tire incorporating chlorinated polyethylene films of the present invention.

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ELASTOMERIC BARRIER FILMS FOR TIRES

This invention generally relates to an elastomeric barrier film as an inner liner, and to pneumatic rubber substrates and rubber tires having such elastomeric barrier film as the inner liner. More
5 particularly, this invention relates to formulated chlorinated polyethylene film as an inner liner, and to the pneumatic rubber substrates and the rubber tires incorporating such a film as an inner liner.

10 Chlorinated polyethylene, particularly chlorinated polyethylene containing from 30 to 50 weight percent chlorine is a useful elastomeric material, and upon being sufficiently cured becomes a rubbery material
15 having improved physical properties such as heat resistance, superior mechanical properties and the like.

It is known that cured or uncured and curable chlorinated polyethylenes (CPE) are useful as rubber
20 materials because of improved properties, in jacketing electrical wires and in hoses because of their excellent heat and oil resistance. However, the utility of chlorinated polyethylenes as inner liners for tires as
25 providing superior air impermeability, heat resistance and other improved mechanical properties has heretofore

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not yet been discovered. It was typically expected that CPE would not have adequate air impermeability or heat resistance for such an application.

5 Pneumatic tires generally have a rubbery elastomeric inner liner which forms the inner surface of the tire. This inner liner is designed to retard or minimize the permeation of air used to inflate the tire, and aid in maintaining the air pressure of the tire. Typically, the inner liner is composed of rubbers which
10 are relatively impermeable to air. Such rubbers include butyl and halobutyl rubbers.

The inner liners based on rubber compositions represent the most expensive component in the tire
15 construction. They also add weight to the tire because relatively thick inner liner coatings are generally necessary to obtain the desired degree of air impermeability. Typically, a butyl rubber liner must be
20 1.5 mm (60 mils) thick to provide the necessary air barrier properties.

The inner liners based on blends of butyl rubber with a natural rubber or reclaimed butyl rubber
25 or both experience difficulty due to diffusion of gases, particularly air through the liner.

U.S. Patent 4,616,687 discloses vulcanizing compositions containing from 80% to 99% rubber material
30 selected from butyl rubber, and halogenated butyl rubber; and 20% to 1% of a chlorinated hydrocarbon polymer having a chlorine content of from 30% to 70% by weight of chlorine. The chlorinated hydrocarbon of this composition is selected from the group consisting of chlorinated polyisoprene having chlorine content from 63

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to 66% by weight, and chlorinated polyolefin having a chlorine content from 30 to about 70% chlorine. However, this composition is composed predominantly of rubber material which is preferably a halobutyl rubber, and the teaching does not address the disadvantages such as cost, weight and the like associated with the use of a predominantly halobutyl rubber liner.

Accordingly, it is an object of present invention to provide an elastomeric film which can be used as an inner liner for rubber tires and which will be more economical and much lighter in weight than butyl or halobutyl rubbers or compositions containing predominantly halobutyl rubber, without losing desired properties such as air impermeability, heat resistance, mechanical properties and the like.

It is yet another object of the present invention to obtain a pneumatic rubber substrate or a tire which incorporates the elastomeric chlorinated polyethylene film of the invention, is light in weight and has the desired properties such as low temperature flexibility, ability to maintain air pressure, and heat resistance.

It has been discovered that films of certain thicknesses fabricated from cured or curable formulated chlorinated polyethylene compositions are useful as inner liners for the rubber tires because of improved air impermeability, heat resistance and good low temperature flexibility. These films, in fact, have oxygen impermeability far superior to that of halobutyl rubber of same thickness.

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In one aspect, the present invention is a two-layered chlorinated polyethylene film for use as an inner liner for a rubber tire comprising an inner layer adjacent an inside surface of the rubber tire containing an adhesive, and an outer layer consisting essentially of 100 parts of chlorinated polyethylene containing from 35 to 50 percent by weight chlorine; a derivative of 2,5-dimercapto-1,3,4-thiadiazole curative; an accelerator; and an acid acceptor. The outer layer, after curing is from 0.13 mm (5 mils) to 0.76 mm (30 mils) in thickness and has oxygen permeability from 6×10^{-12} to 36×10^{-12} cc-cm/cm²-cmHg-sec (10 to 60 cc-mil/100 sq.in.-atm-day).

In still another aspect, the present invention is a curable chlorinated polyethylene film containing carbon black, for use as an inner liner for a rubber tire, comprising at least two layers: an inner layer adjacent an inside surface of said rubber tire comprising a thermoplastic elastomer; and an outer layer of curable chlorinated polyethylene consisting essentially of 100 parts of CPE containing from 35 to 50 percent by weight chlorine; a derivative of 2,5-dimercapto-1,3,4-thiadiazole curative; an accelerator; and an acid acceptor. The outer layer, after curing is from 0.20 mm (8 mils) to 0.51 mm (20 mils) in thickness and has oxygen permeability from 6×10^{-12} to 24×10^{-12} cc-cm/cm²-cmHg-sec (10 to 40 cc-mil/100 sq.in.-atm-day).

This invention, in still another aspect, is a pneumatic rubber article comprising a rubber substrate and an inner liner of a curable chlorinated polyethylene films of the compositions described hereinabove.

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The invention will be more readily understood by reference to the drawings wherein:

Fig. 1 is a cross-sectional view of a tire having an inner liner according to this invention.

5

Fig. 2 is a cross-sectional view of one of the embodiments of the inner liner of this invention.

The composition used in fabrication of the elastomeric films of this invention contains chlorinated polyethylene which can be obtained by after-chlorination of polyethylene by known methods such as by reaction of chlorine or chlorine generating agents with the polyethylene. The polyethylene can be either the low density, or a linear low density, or a high density polyethylene. Typically, the resins are prepared from high density polyethylene feedstock having a melt index of about 6.0 gms/10 minutes. Preferably, compositions with chlorinated polyethylene containing from 20 to 50% by weight chlorine is used. More preferably, chlorinated polyethylenes containing from 40 to 50% chlorine are used. Most preferred compositions are those which consist of chlorinated polyethylenes containing from 42 to 47% chlorine.

The crosslinking systems used to cure the composition are nonsulfur crosslinking systems formulated to cure through the chlorine functionality with dimercapto compounds such as 2,5-dimercapto-1,3,4-thiadiazole, trithiocyanuric acid, dimercaptohydantoins or dimercaptotrizole as disclosed in U.S. Patent 4,128,510 or U.S. Patent 4,288,576 incorporated herein by reference.

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Preferably, the curing agent used is a derivative of 2,5-dimercapto-1,3,4-thiadiazole commercially available as ECHO*, a trademark of Hercules, Incorporated, in amounts from 0.75 parts to 5 parts per 100 parts of chlorinated polyethylene. Most
5 preferably, amount of 2,5-dimercapto-1,3,4-thiadiazole used is about 2 parts per hundred parts of chlorinated polyethylene.

Typically, the crosslinking accelerator used in
10 this invention is a condensation product of aniline with an acyclic aliphatic mono-aldehyde such as butyraldehyde-aniline, acetaldehyde-aniline and the like.

The preferred amount of the accelerator used is from 0.25 parts to 2.0 parts per 100 parts of chlorinated polyethylene. Most preferably,
15 butyraldehyde-aniline, sold under the name BEUTENE*, a trademark of Uniroyal Chemical Company, Inc., in amounts
20 of 0.8 parts per 100 parts of chlorinated polyethylene is used.

The acid acceptor used in this invention is selected from the group consisting of the oxides,
25 hydroxides, carbonates, borates of a metal of Group II of the Periodic Table of Elements. Preferably, the compounds of metals such as magnesium, calcium, and barium may be used. Most preferably, magnesium
30 hydroxide is used both as an acid acceptor and as a stabilizer for processing stability and improved long-term high heat exposure. The preferred amounts of magnesium hydroxide used are from 2 to 10 parts per hundred parts of chlorinated polyethylene. Most preferably, 5 parts of magnesium hydroxide per hundred

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parts of chlorinated polyethylene are used in the formulation of the composition of this invention.

The compositions of this invention may further contain various additives known in the art, such as, 5 antioxidants, pigments, fire retardants, adhesives, and processing aids such as DYNAMAR* PPA 790, a trademark of 3M Company.

Carbon black may optionally be used as an 10 additive in amounts from 20 parts to 50 parts per 100 parts of chlorinated polyethylene. The use of carbon black imparts abrasive resistance to the film and enhances the air impermeability of the film. However, 15 the use of carbon black adversely affects the low temperature flexibility of the film which is a prerequisite for proper functioning of the inner liner film. This can be circumvented by laminating or coextruding the carbon black containing chlorinated 20 polyethylene film of the present invention with an elastomeric layer.

Preferably, the film containing carbon black will be a multi-layered film having a core barrier layer 25 of elastomeric chlorinated polyethylene of the present invention, an inner most adhesive layer adjacent the inside surface of the rubber substrate and an intermediate elastomeric layer interposed between the core layer and the adhesive layer.

30 The inner most adhesive layer will suitably comprise adhesive resins which are curable and well suited for the curing process that takes place when the inner liner is incorporated into the tire. Preferably, the adhesive resin is selected from a group consisting

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of styrenic block copolymers, such as styrene-butadiene copolymers, and styrene-isoprene copolymers; and ethylene-vinyl acetate copolymers (EVA); or a blend of EVA and styrenic block copolymers. Any suitable curable adhesive which has the required ability to prevent
5 delamination of the liner from the tire under the normal operating conditions of the tire can also be used.

The intermediate layer will comprise a thermoplastic elastomer selected from styrenic block
10 copolymers as described hereinabove. The layer containing the thermoplastic elastomer may act as an adhesive layer on curing of the film, thereby eliminating the need for the innermost adhesive layer.
15 The film may optionally have an outermost layer, adjacent the barrier layer, which is preferably but not essentially identical to the thermoplastic elastomer of the intermediate layer.

The chlorinated polyethylene films of this invention may be produced by first mixing the above described components using a Banbury internal mixer, two-roll mill, extrusion mixing device, or other
20 conventional continuous or semi-continuous mixing techniques known in the industry. The pre-mixed
25 compound may (or may not) then be sheeted out on a roll mill to further homogenize the composition. During these processes, the temperature must be kept between 93-121°C (200-250°F) to prevent premature curing or
30 scorching. A rubber calender is then used to fabricate the homogenized compound into a thin sheet of the desired thickness. An uncured calendered chlorinated polyethylene sheet is thus obtained.

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Alternatively, the uncured or curable chlorinated polyethylene films of this invention may be fabricated by mixing and homogenization of the components of the formulation in a single-screw rubber extruder, twin-screw extruder, or other continuous mixing device at temperatures which allow for good mixing without causing premature curing or scorching. The homogenized mixture may then be fabricated through a conventional sheeting die into an uncured or curable CPE film.

Adhesion of the CPE film to the tire under operating conditions is essential to prevent delamination thereof which would lead to undesirable properties such as: 1) poor low temperature properties such as crack formation, 2) development of flat spots in the tire, and 3) non-uniform heating of the tire resulting in an uneven heat build-up in different regions of the tire which could result in the blow-up of tires. Normal operating conditions involve considerable flexure and a broad range of temperature variations.

To achieve an improvement in the adhesion of uncured CPE film to the tire, the films of the present invention will have an inner adhesive layer adjacent the inner surface of the rubber substrate. The adhesive layer will suitably comprise adhesive resins which are curable and well suited for the curing process that takes place when the inner liner is incorporated into the tire. Preferably, the adhesive resin is selected from a group consisting of styrenic block copolymers, such as styrene-butadiene copolymers, and styrene-isoprene copolymers; and ethylene-vinyl acetate

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copolymers (EVA); or a blend of EVA and styrenic block copolymers.

5 The adhesive layer is applied to the uncured chlorinated polyethylene sheet obtained as described hereinabove either through coextrusion techniques using feedblock or multimanifold die technology, or through secondary lamination or coating process.

10 Referring to the Figures, Figure 1 shows a cross-sectional view of a tire having an inner liner of this invention wherein the tire is generally shown at 1, internal space of the tire at C, the tread portion at 2, a reinforcing belt is shown at 13 (as would be used in a bias belted or radial tire), a sidewall at 3, an annular
15 bead at 4 and the inner liner generally by 6, a reinforcing body ply (not shown) extending from one annular bead to the other. The inner liner 6 is made up of an outer CPE layer 8 of the invention, and an inner
20 adhesive layer 7 and extends from one annular bead 4 to the other, preferably ending in the region of the bead at 5.

25 Fig. 2 illustrates one of the embodiments of the inner liner made from CPE film containing carbon black having a core barrier layer of CPE 8, an innermost adhesive layer 7 adjacent the inner surface of the tire carcass and an intermediate elastomeric layer 9
30 interposed between said adhesive layer 7 and said CPE layer 8. Another embodiment of the inner liner made from CPE film containing carbon black, may optionally have an outermost elastomeric layer (not shown), adjacent the barrier layer 8 disposed towards the internal space C of the tire.

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The uncured multi-layered chlorinated polyethylene film containing carbon black is prepared either through coextrusion techniques using feedblock or multimanifold die technology, or through secondary lamination or coating process.

5

The inner liners or the uncured and curable laminated chlorinated polyethylene films of the present invention are incorporated into the tire by well known tire assembly procedures. The inner liner is cured when the vulcanization of the tires is carried out. During the curing process, the outer layer containing chlorinated polyethylene is stretched out to a thickness from 0.12 mm (5 mils) to 0.76 mm (30 mils). The inner liner can be independently cured if desired.

10
15

The films or liners on curing become cross-linked which results in improvement in the properties such as elasticity, resiliency, compression set, dimensional stability, solvent resistance, and barrier properties, all of which are crucial to the proper functioning of the tires.

20

This invention is illustrated by the following examples in which parts are given in weight per hundred parts of chlorinated polyethylene.

25

Example 1

One hundred parts of chlorinated polyethylene, commercially available as TYRIN*, a Trademark of The Dow Chemical Company containing 42% of chlorine by weight were combined with, 2 parts of a derivative of 2,5-dimercapto-1,3,4-thiadiazole commercially available as ECHO*, a Trademark of Hercules Incorporated, 5 parts of magnesium hydroxide commercially sold as STAN MAG*, a

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trademark of Harwich Chemical Corporation, 0.8 parts of
an accelerator butyraldehyde-aniline sold under the name
BEUTENE*, a trademark of Uniroyal Chemical Company, Inc.
and 0.5 parts of a processing aid commercially available
as DYNAMAR* PPA 790, a trademark of 3M Company in a
5 container and mechanically mixed. The processing aid
facilitates removal of the film from the mold. The
mixture was thoroughly homogenized in a BR Banbury
internal mixer. The mixing was allowed to continue
10 until the temperature reached 104°C (220°F).

The homogenized mixture was then sheeted out on
a cool 15.2 cm x 33 cm (6"x13") two-roll mill. A thick
non-uniform sheet commonly known as a "thick blanket"
15 was first produced which was run through the mill three
times to homogenize and stretch it further.

Curing of these sheets was accomplished by
using compression molding techniques using a 90 metric
ton (100 ton) hydraulic press, at 160°C (320°F) at a
20 pressure of 25.5-27.3 metric tons (28-30 tons) for 20
minutes. The films were stretched to a desired
thickness during the curing process.

Oxygen permeability of the sample was measured
25 on an OxTran 1050 permeability tester at -5°C (23°F)
according to ASTM 3985.

Low temperature flexibility was determined with
30 the environmental Instron at -40°C by using 10.1 cm x
10.1cm (4" x 4") squares of film. The Instron jaw span
was set to 7.6 cm (3") for easy loading of the sample.
This allowed for 1.3 cm (1/2") of the sample to be
placed into the top jaws and 1.3 cm (1/2") into the
bottom jaws. The samples were given several minutes to

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5 equilibrate at -40°C before subjecting them to cycling process. Each cycle consisted of the jaw span being closed to 1.9 cm (3/4") and opening again to the 7.6 cm (3") span. This was accomplished using the extension cycle feature of the Instron. Frequency of the test was 4.25 cycles per minute. Each sample was allowed to run for 4 hours (1000 cycles) or until fracture occurred. Results are shown in Table 1 below.

10 Example 2

Example 1 was repeated except chlorinated polyethylene containing 46.5% by weight of chlorine was used. The chlorinated polyethylene used was prepared by known methods with the results again shown in Table 1.

15 Examples 3 and 4

20 Examples 1 and 2 were repeated in generally the same way except 40 parts per hundred parts of chlorinated polyethylene, of carbon black N 650, commercialized by Sid Richardson Carbon and Gasoline Company, having a particle size in the range of 49-60 nanometers were mixed and thoroughly homogenized with the composition in the Banbury internal mixer, before
25 the mixture was sheeted out. The results are summarized in Table 1.

Example 5 and 6

30 To illustrate improved low temperature flexibility of chlorinated polyethylenes by lamination with rubbery skin layers, the cured films of examples 3 and 4 were laminated between two 0.26 mm (10 mils) thick films of ELVAX 3190, Trademark of E.I. Dupont de Nemours & Co., Inc., by compression molding press at 121°C

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(250°F) and pressure of 2.7 metric tons (3 tons) for two minutes. The EVA/CPE/EVA laminates were then tested for low temperature flexibility using the conditions described hereinabove. The results are summarized in Table 1.

5

Specifically, oxygen permeability values and low temperature flexibility results of the six films or Examples 1-6, about 0.31 mm (12 mil) in thickness, along with those for butyl rubber 1.5 mm (60 mil) thick are illustrated in Table I.

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Table 1

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	<u>Sample</u>	<u>Thickness</u>		<u>Oxygen</u>		<u>Normalized</u>		<u>Low</u>
		<u>(mils)</u>	<u>(mm)</u>	<u>Rate</u>	<u>Rate</u>	<u>Oxygen</u>	<u>Permeability</u>	
				<u>(*)</u>	<u>(***)</u>	<u>(**)</u>	<u>(****)</u>	<u>Temperature</u>
								<u>Flexibility</u>
								<u>at -40°C</u>
1	Butyl rubber	60	1.52	3.05	7.22	183	109.8	Passed
	<u>Example 1</u>							
	With No	12.5	0.32	3.04	7.13	38	22.8	Passed
1	Carbon Black	11.4	0.29	3.28	7.66	37	22.2	Passed
	<u>Example 2</u>							
	With No	11.1	0.28	4.70	11.1	52	31.2	Passed
1	Carbon Black	11.8	0.30	4.20	10.0	50	30.0	Passed
	<u>Example 3</u>							
	With Carbon	11.6	0.29	2.83	6.83	33	19.8	Failed
2	Black	12.3	0.31	3.03	7.16	37	22.2	Failed
	<u>Example 4</u>							
	With Carbon	8.5	0.22	2.83	6.55	24	14.4	Failed
2	Black	9.8	0.25	2.62	6.24	26	15.6	Failed
	<u>Example 5</u>							
	EVA/Film of							
2	Ex. 3/EVA	12.2	0.31	2.87	6.77	35	21.0	Passed
	<u>Example 6</u>							
	EVA/Film of							
2	Ex. 4/EVA	16.6	0.42	1.51	3.57	25	15.0	Passed

*cc/100 sq. in.-atm-day
 **cc-mil/100 sq. in.-atm-day
 ***10-10cc/cm²-cmHg-sec
 ****10-12cc-cm/cm²-cmHg-sec

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Example 7

5 An experiment was conducted to illustrate improvement in adhesion of uncured chlorinated polyethylene films of this invention to a tire carcass compound when such films were laminated with different adhesive compositions.

10 0.5 mm (twenty mil) plaques of the uncured tire carcass compound were molded in a compression molding press. 0.5 mm (twenty mil) plaques of uncured chlorinated polyethylene formulation of Example 2 and different adhesive compositions were also molded in a compression molding press using varying conditions
15 depending upon the particular adhesive composition used. A fine mesh cloth backing was applied to the outer surface of both the tire carcass compound and the laminated chlorinated polyethylene film (laminate).
20 This is necessary to prevent stretching of the compositions during adhesive bonding tests. The tire carcass compound and the laminate were sandwiched together with adhesive layer facing the tire carcass compound, and molded in compression molding press at
25 135°C (275°F) and pressure of 0 tons for 10 minutes.

30 The adhesion strength of these laminates was tested by cutting the molded plaques into 1.3 mm (1/2") wide strips. The strips were then placed in an Instron tensile tester and pulled apart using a 180 degree peel test at a rate of 200 mm/minute. The adhesion strength reported in Kg/cm (lbs/in) width of the tire compound is illustrated in Table II.

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Table II

5		<u>Sample</u>	<u>Adhesion to</u> <u>tire carcass</u> <u>compound</u> <u>(lb/in) (Kg/cm)</u>		<u>Adhesion to</u> <u>Film of</u> <u>Example 2</u> <u>(lb/in) (kg/cm)</u>	
	Control	CPE Films of Example 2	2.5	0.45	Inseparable	
10	S-B / Film of Ex. 2	STEREON ¹ 841A styrene- butadiene copolymer (S-B)	13.8	2.47	8.8	1.57
15	EVA/ Film of Ex. 2	ELVAX ² 3190 ethylene- vinyl acetate copolymer (EVA)	7.0	1.25	11.8	2.11

20 ¹Trademark of The Firestone Synthetic Rubber & Latex Co.

²Trademark of E.I. DuPont de Nemours & Co., Inc.

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1. A curable chlorinated polyethylene film for use as an inner liner for a rubber tire comprising:

5 i) an inner layer to be located adjacent an inside surface of the rubber tire, comprising an adhesive resin capable of maintaining adhesion under normal operating conditions; and

10 ii) an outer layer consisting essentially of:

a) 100 parts of chlorinated polyethylene containing from 35 to 50 percent by weight chlorine;

15 b) from 0.75 to 5.0 parts per 100 parts of chlorinated polyethylene, of a derivative of 2,5-dimercapto-1-3,4 thiadiazole as a curative;

20 c) from 0.25 to 2.0 parts per 100 parts of chlorinated polyethylene, of an accelerator; and

d) from 2.0 to 10.0 parts per 100 parts of chlorinated polyethylene, of an acid acceptor;

25 wherein said outer layer being cured on heating said film, is from 0.13 mm to 0.76 mm in thickness, having

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oxygen permeability from 6×10^{-12} to 36×10^{-12} cc-cm/cm²-cmHg-sec.

2. The curable chlorinated polyethylene film of Claim 1, wherein the adhesive resin is selected from a group consisting of styrenic block copolymers and
5 ethylene-vinylacetate copolymer or blends thereof.

3. A chlorinated polyethylene film for use as an inner liner for a rubber tire, said film having at least two layers, an inner layer and an outer layer;
10

a) said inner layer to be located adjacent an inside surface of said rubber tire comprising a thermoplastic elastomer;

15 b) said outer layer consisting essentially of:

1) 100 parts of chlorinated polyethylene containing from 35 to 50 percent by weight chlorine;

20 2) from 0.75 to 5.0 parts per 100 parts of chlorinated polyethylene, of a derivative of 2,5-dimercapto-1-3,4 mercaptothiadiazole curative;

25 3) from 0.25 to 2.0 parts per 100 parts of chlorinated polyethylene, of an accelerator;

4) from 2.0 to 10.0 parts per 100 parts of chlorinated polyethylene, of an acid acceptor; and

30 5) from 20 parts to 50 parts per 100 parts of chlorinated polyethylene, of carbon black;

wherein said outer layer being cured on heating said film, is from 0.20 mm to 0.64 mm in thickness having

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oxygen permeability from 6×10^{-12} to 24×10^{-12} cc-cm/cm²-cmHg-sec.

4. The curable chlorinated polyethylene film of Claim 3, wherein the thermoplastic elastomer comprises styrenic block copolymers.

5

5. The curable chlorinated polyethylene film of Claim 2 or Claim 4, wherein said accelerator is butyraldehyde-aniline.

10

6. The curable chlorinated polyethylene film of Claim 5, wherein said acid acceptor is magnesium hydroxide.

15

7. A pneumatic rubber article comprising:

a) a rubber substrate and

20

b) a chlorinated polyethylene film as an inner liner adhered to inside surface of said substrate, comprising:

25

i) an inner layer adhered to an inside surface of the rubber substrate, comprising an adhesive resin capable of maintaining adhesion under normal operating conditions; and

30

ii) an outer layer consisting essentially of:

(1) 100 parts of chlorinated polyethylene containing from 35 to 50 percent by weight chlorine;

(2) from 0.75 to 5.0 parts per 100 parts of chlorinated polyethylene, of a derivative of 2,5-dimercapto-1-3,4 mercapto-thiadiazole curative;

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(3) from 0.25 to 2.0 part per 100 parts of chlorinated polyethylene, of an accelerator; and

(4) from 2.0 to 10.0 parts per 100 parts of chlorinated polyethylene, of an acid acceptor;

5 wherein said outer layer being cured on heating said film, is from 0.13 mm to 0.76 mm in thickness and having oxygen permeability from 6×10^{-12} to 36×10^{-12} cc-cm/cm²-cmHg-sec.

10 8. The pneumatic rubber article of Claim 7, wherein the adhesive resin is selected from a group consisting of styrenic block copolymers and ethylene-vinylacetate copolymer or blends thereof.

15 9. The pneumatic rubber article of Claim 8, wherein the film contains from 40-50% by weight chlorine, and said outer layer of the film after being cured on heating is from 0.13 mm to 0.76 mm in thickness
20 having oxygen permeability from 6×10^{-12} to 30×10^{-12} cc-cm/cm²-cmHg-sec.

10. The pneumatic rubber article of Claim 8, wherein said accelerator is butyraldehyde-aniline.

25 11. The pneumatic rubber article Claim 8, wherein said acid acceptor is magnesium hydroxide.

12. The pneumatic rubber article of any of Claims 7 through 11 wherein the rubber substrate is a
30 rubber tire.

13. A pneumatic rubber article comprising:

a) a rubber substrate and

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b) a chlorinated polyethylene film as an inner liner comprising at least two layers:

a) an inner layer adhered to an inside surface of said rubber substrate comprising a thermoplastic elastomer;

5

b) an outer layer consisting essentially of:

(1) 100 parts chlorinated polyethylene containing from 35 to 50 percent by weight chlorine;

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(2) from 0.75 to 5.0 parts per 100 parts of chlorinated polyethylene, of a derivative of 2,5-dimercapto-1-3,4 thiadiazole curative;

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(3) from 0.25 to 2.0 part per 100 parts of chlorinated polyethylene, of an accelerator;

(4) from 2.0 to 10.0 parts per 100 parts of chlorinated polyethylene, of an acid acceptor; and

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(5) from 40 parts to 50 parts per 100 parts of chlorinated polyethylene of carbon black;

wherein said outer layer being cured on heating said film, is from 0.20 mm to 0.64 mm in thickness having oxygen permeability from 6×10^{-12} to 24×10^{-12} cc-cm/cm²-cmHg-sec.

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14. The pneumatic rubber article of Claim 13, wherein said thermoplastic elastomer comprises a styrenic block copolymer.

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15. The pneumatic rubber article of Claim 14 wherein said accelerator is butyraldehyde-aniline.

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16. The pneumatic rubber article of Claim 15,
wherein said acid acceptor is magnesium hydroxide.

17. The pneumatic rubber article of any of
Claims 13 through 16, wherein the rubber substrate is a
rubber tire.

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FIG. 1

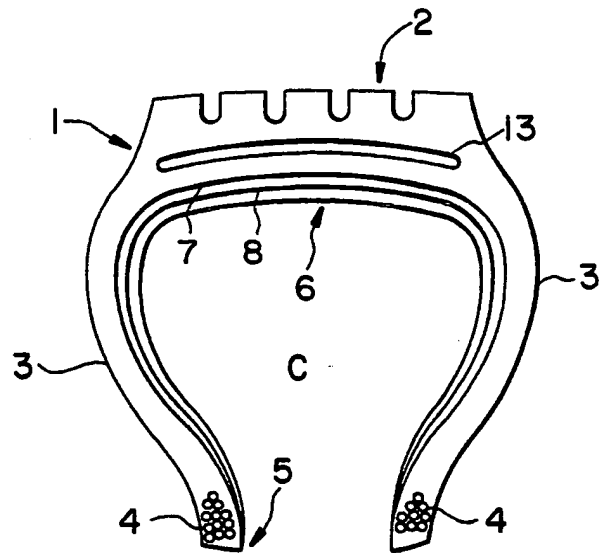
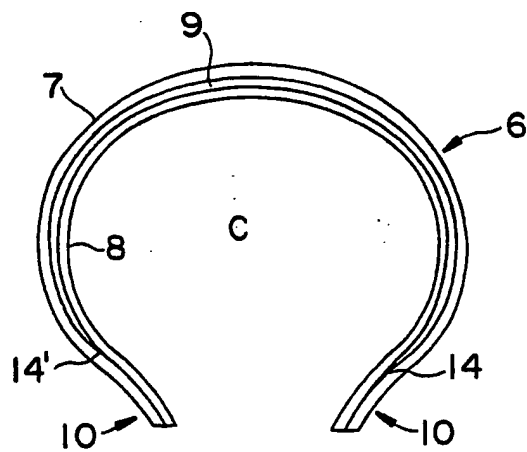


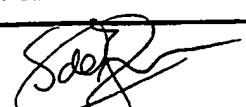
FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 92/02417

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B60C1/00; B32B27/06; C08K5/47		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B60C ; B32B ; C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	FR,A,2 022 364 (THE B.V. GOODRICH COMPANY) 31 July 1970 see claim 1 ---	
A	US,A,3 038 515 (R.C. KOCH ET AL) 12 June 1962 see the whole document ---	
A	US,A,4 549 593 (YAHAGI ET AL) 29 October 1985 see the whole document ---	
A	EP,A,0 201 890 (THE DOW CHEMICAL COMPANY) 20 November 1986 see page 11 - page 12; claim 1 ---	
P,A	EP,A,0 455 030 (RHEIN-CHEMIE RHEINAU RMBH) 6 November 1991 see the whole document ---	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
07 SEPTEMBER 1992	11. 09. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DE JONGE S.J.P. 	

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9202417
SA 61138**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
FR-A-2022364	31-07-70	DE-A-	1954886	06-05-70
		GB-A-	1288080	06-09-72
		NL-A-	6916480	06-05-70
		US-A-	3586087	22-06-71

US-A-3038515		DE-B-	1082823	

US-A-4549593	29-10-85	JP-A-	59120501	12-07-84
		CA-A-	1194767	08-10-85

EP-A-0201890	20-11-86	US-A-	4680234	14-07-87
		AU-B-	566259	15-10-87
		AU-A-	5739486	20-11-86
		JP-A-	61261049	19-11-86
		US-A-	4724186	09-02-88

EP-A-0455030	06-11-91	DE-A-	4013714	31-10-91

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